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Patentanmeldung Nr. Patent application No. Demande de brevet n°

03405403.1

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High-resolution patterning

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HIGH-RESOLUTION PATTERNING

TECHNICAL FIELD

The present invention is related to a method for forming a pattern on a surface by deposition of a mixture that comprises an application material and a phase-change transfer material and a composition for patterning a surface. Further, the invention is related to a process for fabricating an organic light-emitting device (OLED) and in particular to high-resolution patterning for RGB displays.

BACKGROUND OF THE INVENTION

Organic light-emitting devices (OLEDs) are commonly manufactured as a sequence of layers deposited on top of each other such as a first electrode on a supporting substrate, several organic and inorganic layers and a second electrode. So far, OLED technology is lacking a high-resolution patterning method for RGB displays for small molecules. The deposition technologies developed for small molecules so far show limitations for mass production of large-sized displays.

Conventionally, vacuum evaporation is employed as the physical vapor deposition method in forming the organic layers. A common method for patterning of the organic layers e.g. for red, green and blue emitting sub-pixels in a full-color display, is the shadow mask technique. However, this technique is limited in size, resolution of the panel, and the individual fill-factor of the pixel. For example, shadow mask technology becomes extremely complicated in particular for small feature sizes. The material deposition during the process requires regular mask cleaning steps which delay the manufacturing. Thermal expansion of the mask during the deposition limits the precision and aperture ratio. Moreover, repeatedly necessary mask alignment is time consuming and reduces yield.

A method used for patterning polymer light-emitting devices is ink-jet printing of dissolved polymers as described in US patent 6,087,196. This method of dispensing a liquid solution is not suitable for multi-layer OLEDs based on small molecules because

previously deposited layers are re-dissolved and intermixed by the sequential deposition of multiple layers from different solutions.

From the above follows that there is still a need in the art for improved patterning of structures for the fabrication of semiconductor devices, sensors, biochips, and displays

- 5 using organic and/or inorganic active or biological layers.

SUMMARY AND ADVANTAGES OF THE INVENTION

The present invention allows the fabrication of semiconductor devices, circuits, sensors, biological patterns, biochips, and displays using organic and/or inorganic active or biological layers. The method involves the deposition of molecules, oligomers or 5 nanoparticles added to a transfer material by a phase-change printing technique and the fabrication of organic light-emitting devices, color displays and other semiconductor devices.

In accordance with the present invention, there is provided a method for forming a pattern on a surface by deposition of a mixture that comprises an application material 10 and a phase-change transfer material. The method comprises the steps of heating the mixture to a melt; depositing the melted mixture on the surface with a phase-change printing technique, thereby the melted mixture solidifies instantaneously when it reaches the surface; and removing the transfer material.

In accordance with another aspect of the present invention, there is provided a process 15 for fabricating an organic light-emitting device (OLED). The process comprises the steps of heating a composition to a melt, the composition comprises an organic material and a phase-change transfer material; depositing the melted composition onto a surface by a phase-change printing technique, thereby the melted composition solidifies instantaneously when it reaches the surface; and removing the transfer material whereby 20 the organic material remains on the surface.

In general, the present invention relates to a way of high-resolution patterning of layers, for example with organic molecules, by a phase-change printing technique, also referred to as wax printing technique, for the use in semiconductor devices, sensors, or color displays. One or more species or mixtures of organic molecules, oligomers, or 25 nanoparticles, each also referred to as application material, is/are added to a transfer material, that in its normal state is a "wax". The transfer material is preferably solid at approximately 0 °C and ambient temperature and melts under ambient pressure below 200 °C. The transfer material sublimes, preferably under reduced pressure, from the solid to the gaseous state at a temperature below 200 °C. An example for a transfer material

could be cyclododecane and its derivatives. The transfer material cyclododecan is such a transfer material which is solid at room temperature, melts at about 60 °C and disappears under vacuum conditions without going into the liquid phase. Additionally, it is hydrophobic and thus ideal for mixing with OLED materials. This material could be used
5 as a wax where organic host, and guest-host systems could be doped in.

Prior to deposition, the mixture of transfer material, that is a wax, and application materials or a part thereof is heated to the melting temperature of the transfer material and deposited onto a substrate or surface, e.g. a thin film transistor array for a full-color display. The deposition of the melted mixture can be performed by a thermal
10 phase-change printing technique. The mixture of "wax" and application materials solidifies immediately when it hits the substrate. The transfer material, that is a phase-change material, can be removed by sublimation and a patterned layer of the active materials remains on the substrate. The sublimation can be accelerated if the substrate is heated and/or evacuated. The deposition can be repeated to cast multiple layers on top of
15 each other. The combination of both low pressure and temperature seems to be the most efficient. It is advantageous that the transfer material sublimes from solid state to vapor state without forming a liquid, because then the deposited structure remain exactly as desired and the pattern does not blur.

The steps of the method and process can be repeated to deposit multiple layers, i.e. more
20 than three layers can be formed easily. It addition it might be advantageous to deposit first all or some of the desired layers of application material and then second to remove the respective transfer material of the various layers at once.

In accordance with a further aspect of the present invention, there is provided a composition for patterning a surface. The composition, also referred to as mixture or
25 phase change ink, comprises an application material for forming a pattern, and a phase-change transfer material that sublimates after patterning by an action. The action can be a heating, the application of low pressure, and the combination thereof. The action that involves a physical effect can also involve the application of light with a defined wavelength in order to remove the transfer material. This may help to ease the
30 removal process of the transfer material.

In contrast to conventional phase-change or wax printers where the wax is used as material which is transferred and sticks to the surface, the transfer material, i.e. the wax, here is used as transfer medium where the application material, for example with organic molecules, is comprised therein.

- 5 The composition can be a mixed powder. This has the advantage that it can be easily mixed with further components or the concentration between the application material and the transfer material can be adapted or changed. In a preferred example the concentration between the application material and the transfer material is 1:100. In other examples the ratio might be 1:1 or even 1:10.000 or larger. This depends on the
- 10 application and the field of application, e.g., using biological material may demands a different ratio then using nanoparticles.

The thickness of each layer created by the phase-change printing can be defined by the ratio between the application material and the transfer material.

- 15 The mixing of the application material with the transfer material to the mixture or composition can be performed by mixing powders. In a further embodiment, the transfer material is heated to its melting point and then the application material is added. It might be also advantageous if the application material and the transfer material are mixed together not until the mixture is to be deposited to the surface. That means, just before the deposition of the mixture takes place the materials are mixed and heated for the
- 20 application. By doing so, two or more separate containers can be used and filled individually.

The transfer material can comprise one or more components which enhance the transfer process. For example, a wax forming material can be combined with a material wherein molecules have an excellent solubility.

- 25 The application material can comprise one of an organic material, an OLED material, biological molecules, nano-particles, or a combination thereof.

- A field-effect transistor, also referred to as thin-film field-effect transistor, can be made by a process comprising the steps of forming source and drain contacts on a substrate; heating a composition to a melt, the composition comprises an organic material and a phase-change transfer material; depositing the melted composition onto the substrate
5 with the source and drain contacts by a phase-change printing technique, thereby the melted composition solidifies instantaneously when it reaches the substrate; removing the transfer material whereby the organic material remains on the surface as an organic semiconducting layer; forming an insulating layer on the organic semiconducting layer; and forming a gate contact on the insulating layer.
- 10 It is also possible to form the source, drain, and gate contacts as well as the insulating layer by the phase-change printing technique. This has the advantage that the whole device can be fabricated by the disclosed phase-change printing technique.

DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described in detail below, by way of example only, with reference to the following schematic drawings.

FIGs. 1 a - e illustrate the steps for forming a pattern on a surface by deposition of a mixture that comprises an application material and a phase-change transfer material,

FIGs. 2a, b show a schematic illustration of the formation of organic light-emitting devices,

FIG. 2 c shows a schematic illustration of the formation of an RGB display,

FIG. 3 shows a schematic illustration of the formation of a field-effect transistor.

FIG. 4 illustrates the phase-change printing principle.

The drawings are provided for illustrative purpose only and do not necessarily represent practical examples of the present invention to scale.

DETAILED DESCRIPTION OF EMBODIMENTS

Although the present invention is applicable in a broad variety of applications it will be described with the focus put on an application to an organic electroluminescent device, i.e. an organic light-emitting device (OLED) and a field-effect transistor, but first the 5 general process is addressed. The same reference numbers are used to denote the same parts or the like.

Figs. 1a-e illustrate steps for forming a pattern on a surface 10 by deposition of a mixture 20 that comprises an application material 22 and a phase-change transfer material 24. For the sake of simplicity, the figure is simplified to a droplet. Two or more thereof are 10 contemplated to form a pattern and multiple a layer. Fig. 1a illustrates the mixing of the application material 22 with the transfer material 24 to the mixture 20. As indicated in Fig. 1b, the mixture 20 is heated to a melt 21. Then, as indicated in Fig. 1c, the melted mixture 21 is deposited on the surface 10 by phase-change printing. Thereby the melted mixture 21 solidifies instantaneously when it reaches the surface 10. The mixture 20 or 15 phase-change ink is melted by heating elements and deposited, for example, via piezo elements (not shown). Finally, as indicated in Fig. 1d, low pressure is applied to the solidified or deposited mixture 20 whereby the transfer material 24 is removed by sublimation. It remains the application material 22 on the surface 10 as indicated in Fig. 1e. In order to deposit multiple or various layers of application material, the process 20 steps are repeated. The application material 22 and the transfer material 24 can also be mixed together upon the mixture is to be deposited to the surface. That means, right before the deposition of the mixture takes place the materials are mixed and heated for the application. This allows to use two or more separate containers which can be used, changed, and filled individually. In the Figs. 1a-e, the symbols "x" illustrate the components 25 of the application material 22 and the symbols "o" illustrate the components of the transfer material 24 in solid form whilst the symbols "-" illustrate the components of the transfer material 24 in melted form.

The Figs. 2a to 2c show a schematic illustration of the formation of an organic light-emitting device (OLED). In at least some instance the OLED includes a thin layer, 30 or layers, of suitable organic materials sandwiched between a cathode and an anode. One

suitable example of the OLED is illustrated in Fig. 2a. On a suitable surface of a substrate 100, a first electrode (anode) 102 (metal, ITO, conductive polymer) is provided either by conventional methods, like PVD, CVD, spin coating or sputtering, or by the phase-change printing technique. The substrate 100 can be made of glass, silicon, 5 polymer, or a combination thereof or might even be a pre-patterned thin-film transistor array. The OLED further comprises a hole transport layer 106 and an electron transport/emitter layer 110' and a second electrode (cathode) 112 (metal). Other OLED multi-layer devices may include further layers as depicted in Fig. 2b. Besides the hole transport layer 106 a hole injection layer 104 may be included. The combined electron 10 transport/recombination layer could be separated into an electron transport layer 110 and an emission layer 108. All of those layers can be blends of several materials in particular the emission layer could be a blend of one or several host and dye materials. Thus, such multi-layer OLEDs can be formed on the suitable surface by consecutive casting of individual layers by the phase-change printing method described with reference to the 15 Figs. 1a-e and Fig. 4.

A display can be formed as illustrated in Fig. 2c. Red 302, green 304 and blue 306 OLED pixels may be printed on a receptor substrate 300 by phase-change printing. Alternatively, the red, green and blue OLEDs could be printed on top of each other to create a multi-color stacked OLED device.

20 One example of the formation of a field-effect transistor is illustrated in Fig. 3. Two electrical contacts named source and drain 402 are formed on the surface of an insulating substrate 400 that can comprise glass, silicon, polymer, or a combination thereof. The source and drain 402 can be formed by conventional techniques, e.g. PVD, CVD, sputtering, etc., but source and drain 402 can also be formed by phase-change printing. 25 For the latter, for example, gold nanoparticles are well suited as application material to be mixed with the phase-change transfer material to the mixture that is applied to the surface of the insulating substrate 400. Further, an organic semiconducting layer 404 is applied by phase-change printing between source and drain contacts and overlapping these contacts 402. Pentacene or alpha-sexithiophene can here be used as organic 30 molecules for the application material. An insulating layer 406 is then formed over the semiconducting layer 404, thereby the insulating layer 406 can comprise SiO_2 or Al_2O_3 .

as nanoparticles in the application material for forming the mixture or composition. Finally, a third electrode 408, the gate electrode, is formed on top of the insulating layer 406. The third electrode 408 can be formed like the source and drain 402 and also may comprise nanoparticles of gold. The phase-change printing can be applied to all or 5 several layers of the field-effect transistor.

In fact, one printer with various containers each filled with the respective application material and the transfer material can be used to produce a complete device, like the above-described OLED or thin-film transistor.

Fig. 4 illustrates the phase-change printing principle with its units. A material loader 40, 10 that can be a container or reservoir, is arranged closed to a printhead 44. A direct connection is also possible, e.g. applying capillary action. The material loader 40 comprises a heating element 41 and contains the mixture or composition 20. The printhead 44 can be brought close to the surface 10 of a device or substrate 11. Further, the printhead 44 comprises material jets 46 which work, for example, with piezo 15 elements (not shown) to eject the melted material 21. For applying the application material 20 to the surface, either the printhead 44 is moved over the surface 10 or the printhead 44 is fixed and the substrate 11 with the surface 10 is moved in a way to pattern the surface 10 accordingly. In operation, the heating element 41 melts the mixture 20 at one end of the material loader 40. The melted mixture 21 drains or drips to the 20 printhead 44, that preferably is also heated. Via the material jets 46, the melted material 21 is brought to the surface 10 where the melted mixture 21 solidifies immediately. In a another embodiment, the material loader 40 and the printhead 44 together can also form a single unit. In a further embodiment, multiple of the material loader 40, each filled 25 with a mixture or composition that comprises a different application material 22, can be used to support the printhead 44.

Any disclosed embodiment may be combined with one or several of the other embodiments shown and/or described. This is also possible for one or more features of the embodiments.

CLAIMS

1. A method for forming a pattern on a surface (10) by deposition of a mixture (20) that comprises an application material (22) and a phase-change transfer material (24), the method comprising the steps of:

- 5 b.) heating the mixture (20) to a melt;
 c.) depositing the melted mixture (21) on the surface (10) with a phase-change printing technique, thereby the melted mixture (21) solidifies instantaneously when it reaches the surface (10); and

 d.) removing the transfer material (24).

10 2. The method according to claim 1 further comprising the step of a.) mixing the application material (22) with the transfer material (24) to the mixture (20).

3. The method according the one of the preceding claims, wherein the step of removing the transfer material (24) comprises removing the transfer material (24) by sublimation.

15 4. The method according the one of the preceding claims, wherein the step of removing the transfer material (24) by sublimation comprises applying a low pressure to and/or heating the deposited mixture (20).

5. The method according the one of the preceding claims comprising repeating the steps b.) to d.) to deposit multiple layers.

- 12 -

6. A process for fabricating an organic light-emitting device (OLED) comprising the steps of:

heating a composition (20) to a melt (21), the composition (20) comprises an organic material (22) and a phase-change transfer material (24);

5 depositing the melted composition (21) onto a surface (10) by a phase-change printing technique, thereby the melted composition (21) solidifies instantaneously when it reaches the surface (10); and

removing the transfer material (24) whereby the organic material (22) remains on the surface (10).

10 7. A composition (20) for patterning a surface (10) comprising

an application material (22) for forming a pattern, and

a phase-change transfer material (24) that sublimates after patterning by an action.

8. The composition according to claim 7 being a mixed powder.

9. The composition according to one of the preceding claims 7 and 8, wherein the

15 application material (22) comprises one of an organic material, an OLED material, biological molecules, nanoparticles, and a combination thereof.

10. The composition according to one of the preceding claims 7 to 9, wherein the transfer material (24) is a solid at approximately 0°C and melts at ambient pressure below 200°C.

20 11. The composition according to one of the preceding claims 7 to 10, wherein the transfer material (24) comprises cyclododecane or its derivatives.

- 13 -

12. The composition according to one of the preceding claims 7 to 11, wherein the transfer material (24) comprises one or more components.

13. The method according to claims 1 to 5 used to fabricate one of an organic electronic device, a monochrome and/or color display, a biological pattern, a biochip, a sensor, 5 a semiconductor device, and a circuit.

14. A process for fabricating a field-effect transistor comprising the steps of:

forming source and drain contacts (402) on a substrate (400);

heating a composition (20) to a melt (21), the composition (20) comprises an organic material (22) and a phase-change transfer material (24);

10 depositing the melted composition (21) onto the substrate (400) with the source and drain contacts (402) by a phase-change printing technique, thereby the melted composition (21) solidifies instantaneously when it reaches the substrate (400);

removing the transfer material (24) whereby the organic material (22) remains on the surface (10) as an organic semiconducting layer (404);

15 forming an insulating layer (406) on the organic semiconducting layer (404); and

forming a gate contact (408) on the insulating layer (406).

15. The process according to claim 14, wherein at least one of the source/drain contacts (402), the insulating layer (406), and the gate contact (408) is created according to the method of claims 1 to 5 by the phase-change printing technique.

ABSTRACT

The present invention describes a method to pattern layers of organic and/or inorganic or biological molecules by a printing technique for the use in semiconductor devices, circuits, sensors, biological patterns, biochips, and displays using organic and/or

5 inorganic active or biological layers. One or more species or mixtures of organic molecules, oligomers or nanoparticles are added to the phase-change transfer material.

Prior to deposition, the mixture of transfer material and organic molecules or a part of it is heated to the melting temperature of the phase-change material and deposited onto a substrate e.g. a thin film transistor array for a full-color display. The mixture of

10 phase-change material and organic molecules solidifies instantaneously when it hits the substrate. The phase-change material can be removed by sublimation and a patterned layer of organic and/or inorganic or biological molecules remains on the substrate. The deposition can be repeated to cast multiple layers on top of each other.

[Fig. 1]

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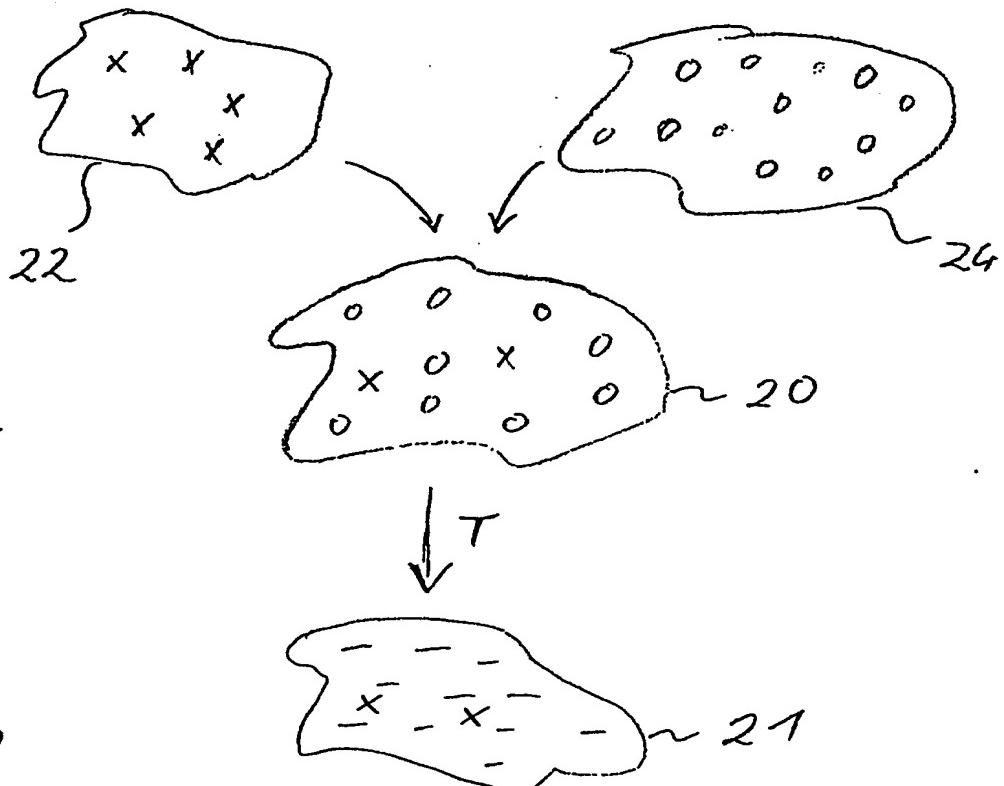


Fig. 1c

Fig. 1d

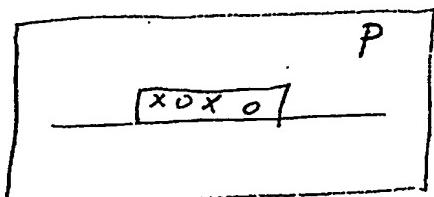
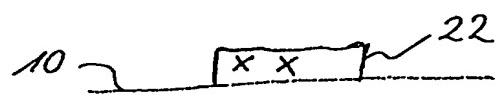


Fig. 1e



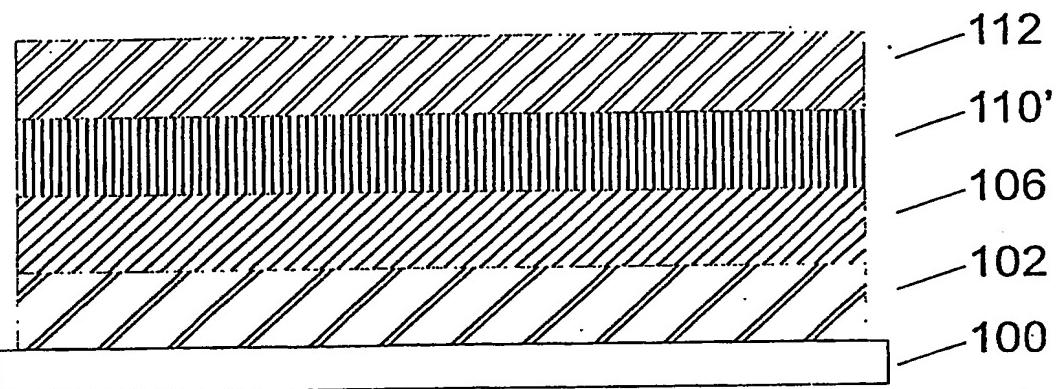


Fig. 2a

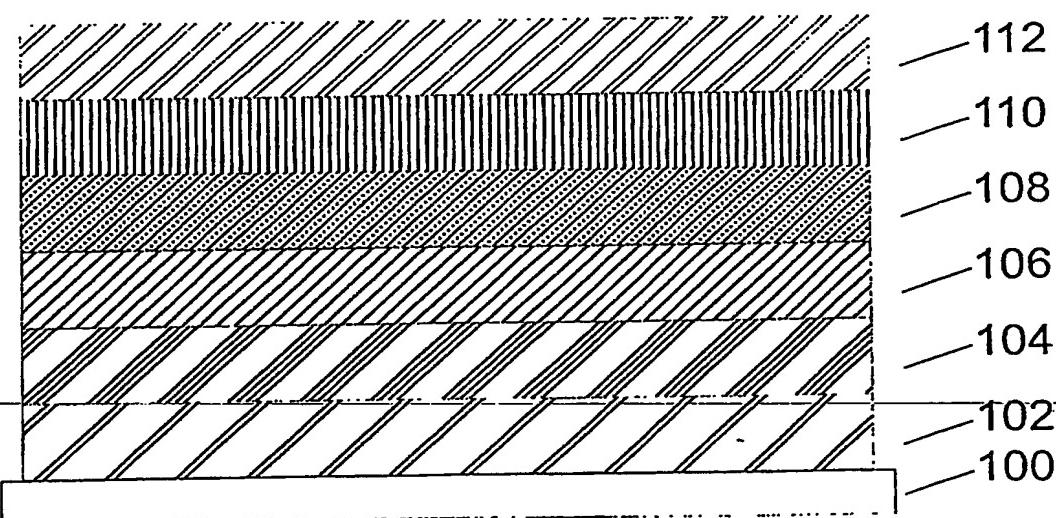


Fig. 2b

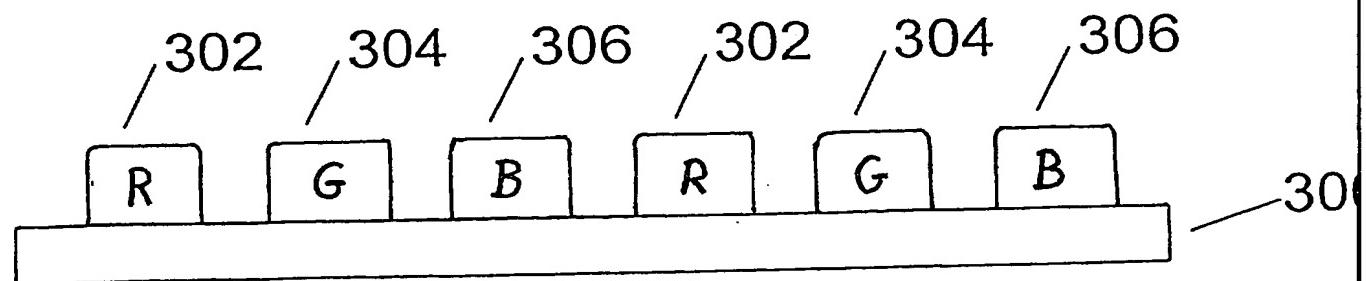


Fig. 2c

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3/3

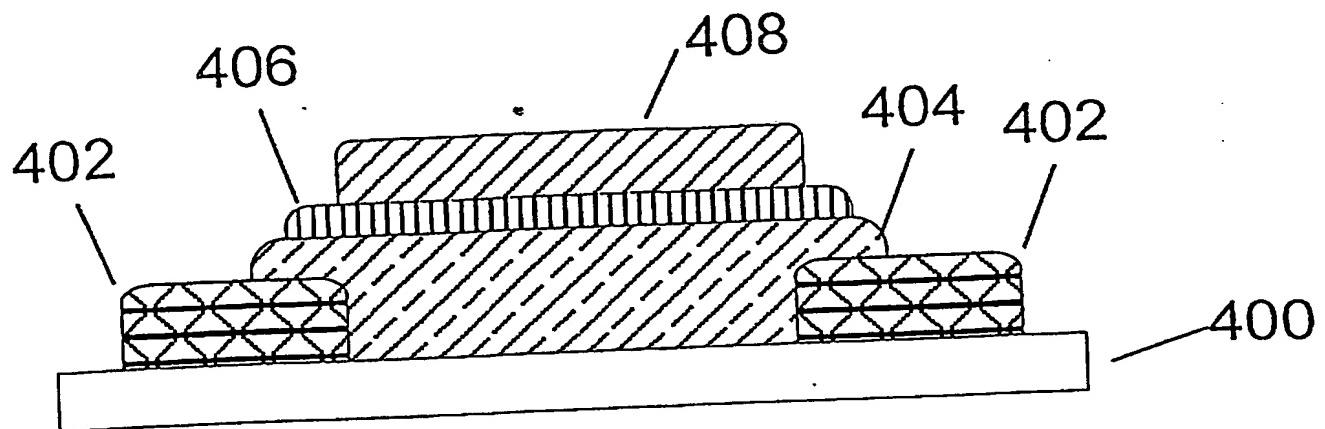


Fig. 3

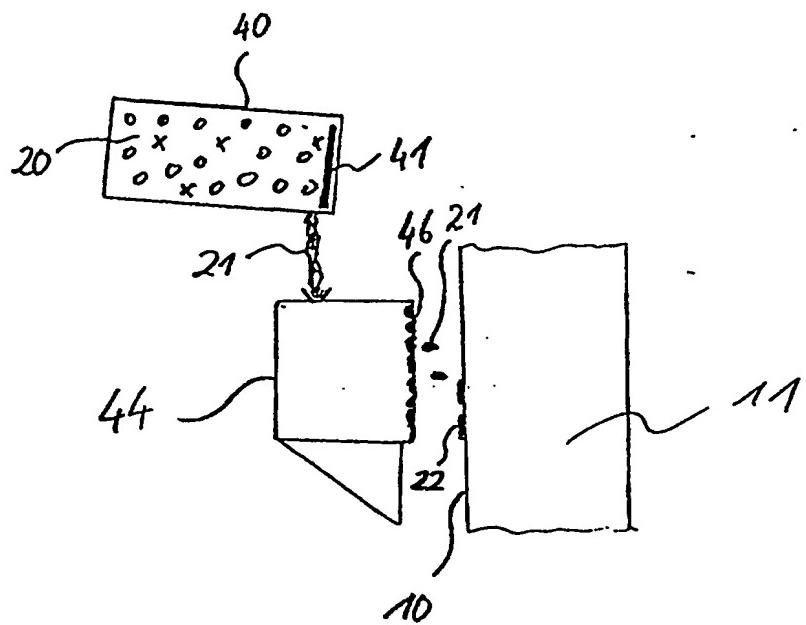


Fig. 4

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